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(54) **METHODS FOR FABRICATING METAL NANOWIRES**

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(51) **Int. Cl.**⁷ **C25D 1/04**

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(58) **Field of Search** **205/76, 109, 122, 205/104**

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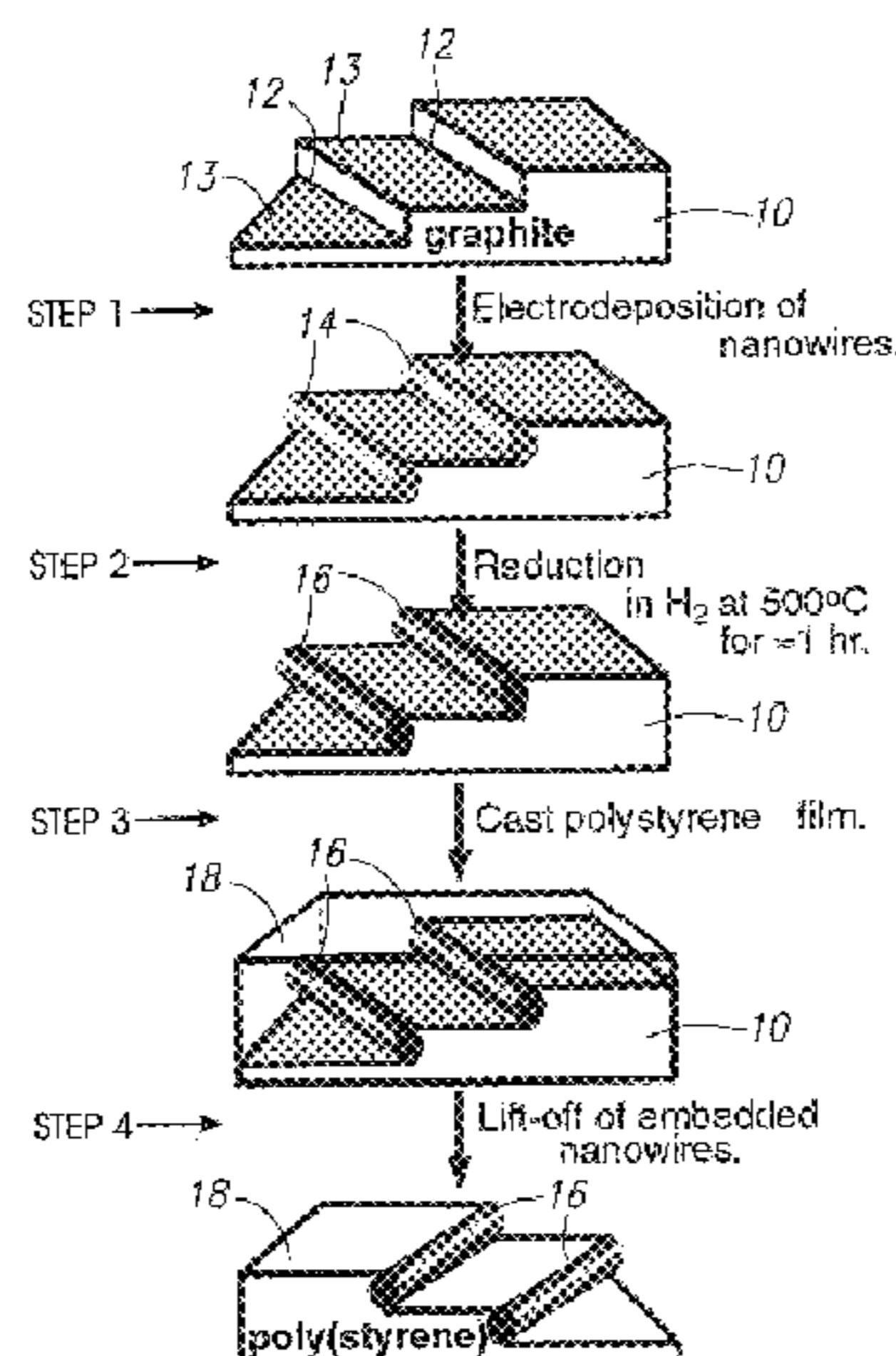
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(57) **ABSTRACT**

Methods for the preparation of long, dimensionally uniform, metallic nanowires that are removable from the surface on which they are synthesized. The methods include the selective electrodeposition of metal nanowires at step edges present on a stepped surface, such as graphite, from an aqueous solution containing a metal or metal oxide. Where a metal oxide is first deposited, the metal oxide nanowires are reduced via a gas phase reduction at elevated temperatures to metal nanowires. Alternatively, beaded or hybrid nanowires comprising a metal A into which nanoparticles of a metal B have been inserted may be prepared by first electrodepositing nanoparticles of metal B selectively along step edges of a stepped surface, capping these nanoparticles with a molecular layer of an organic ligand, selectively electrodepositing nanowire segments of metal A between nanoparticles of metal B and then heating the surface of the hybrid nanowire under reducing conditions to remove the ligand layer. In all three methods, the nanowires may be removed from the stepped surface by embedding the wires in a polymer film, and then peeling this film containing the embedded wires off of the stepped surface.

19 Claims, 8 Drawing Sheets



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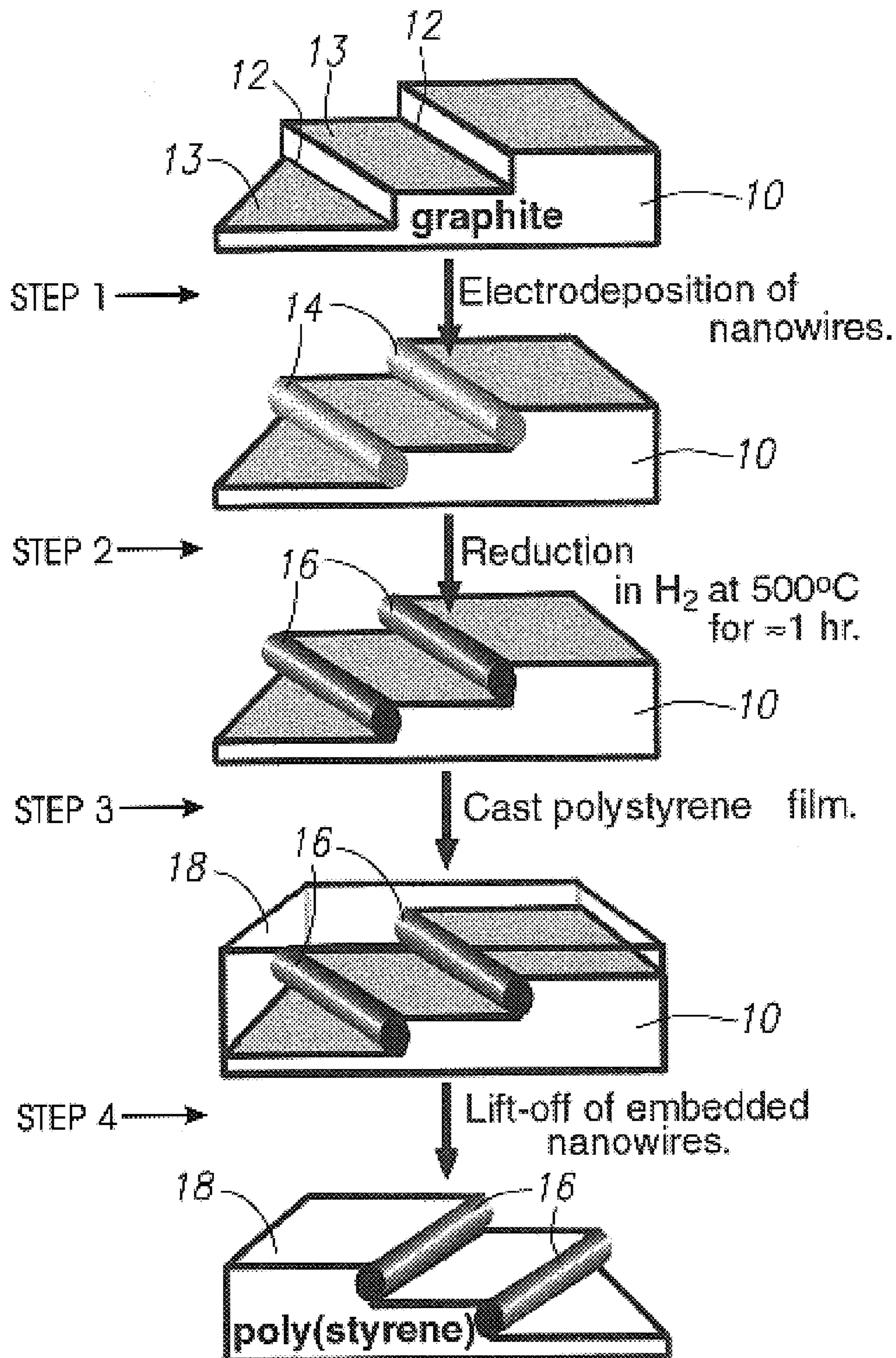


FIG. 1

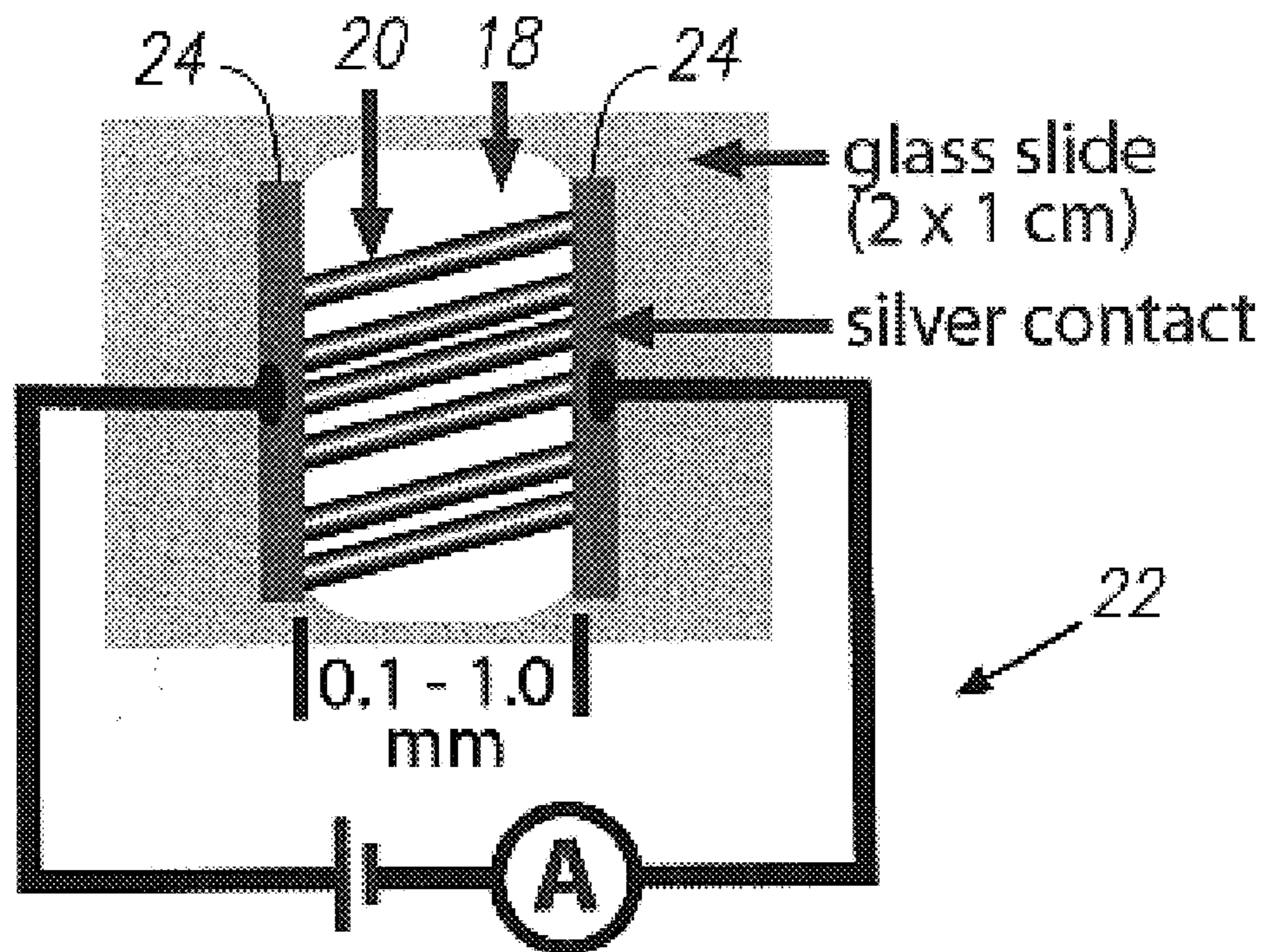


FIG. 2

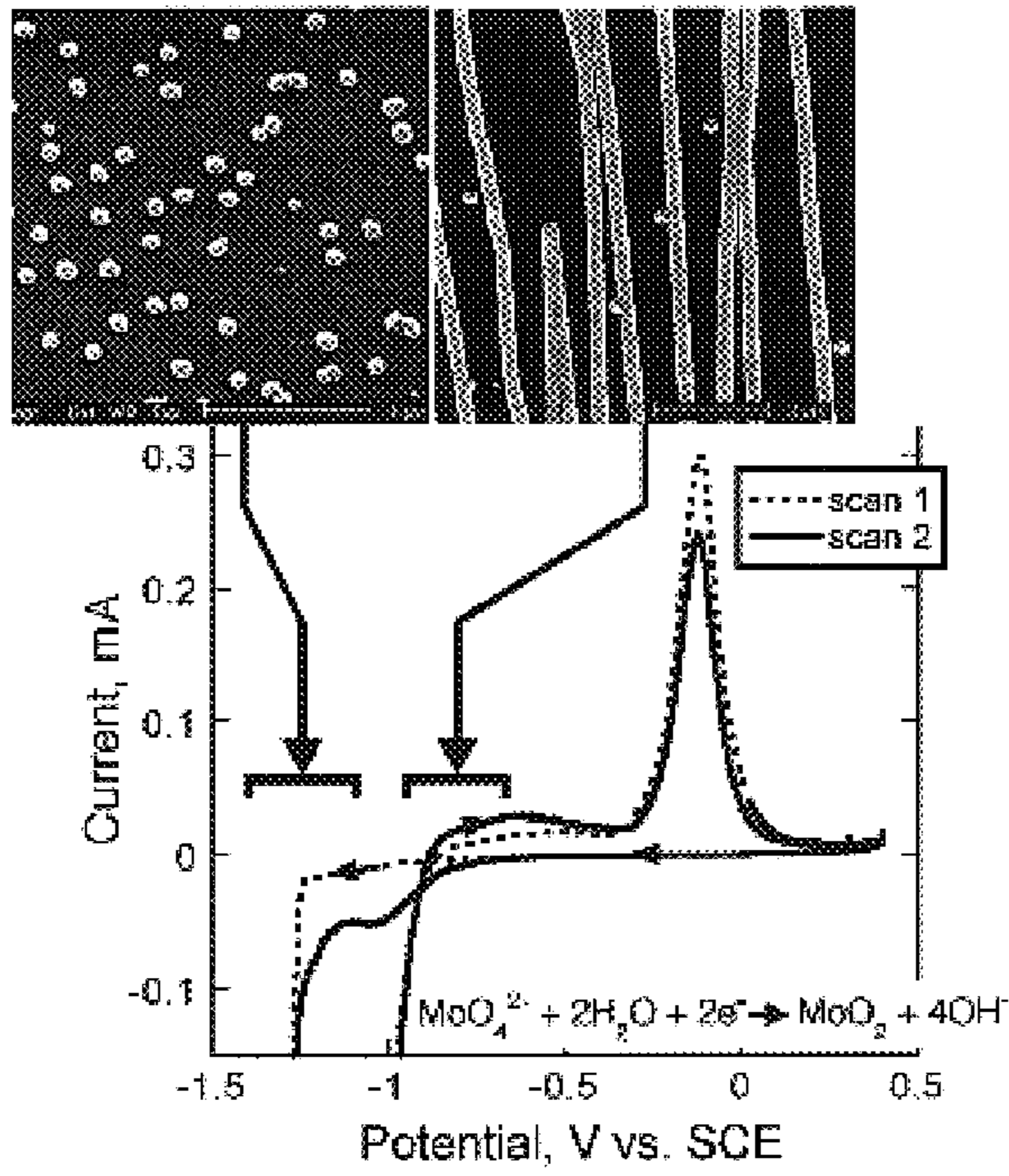


FIG. 4

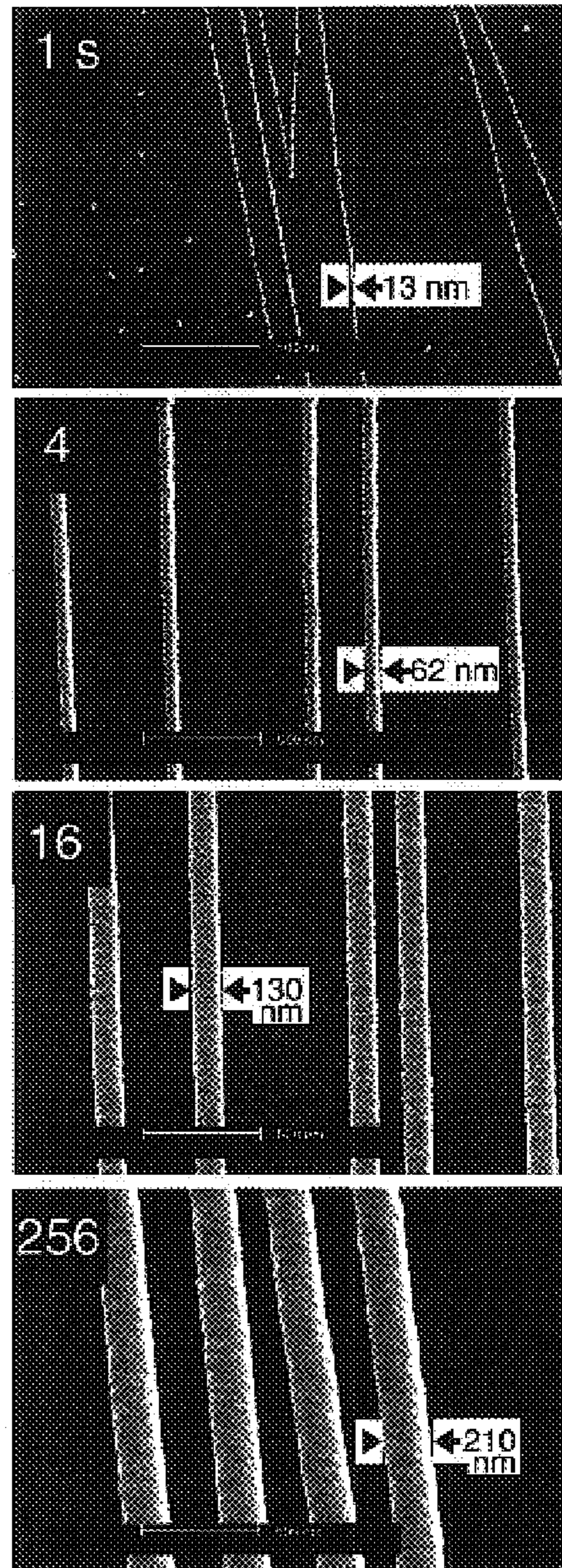


FIG. 3

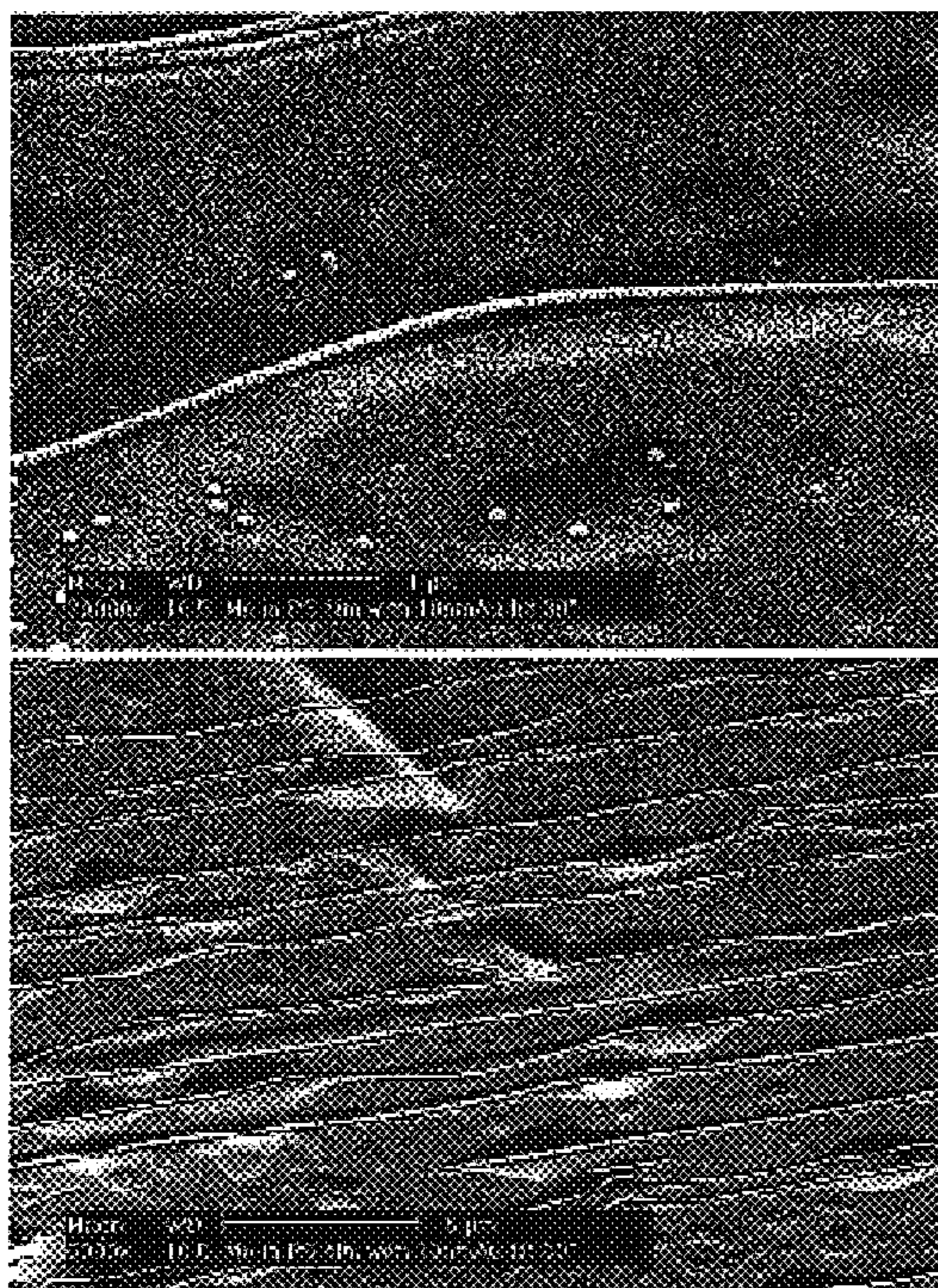


FIG. 5

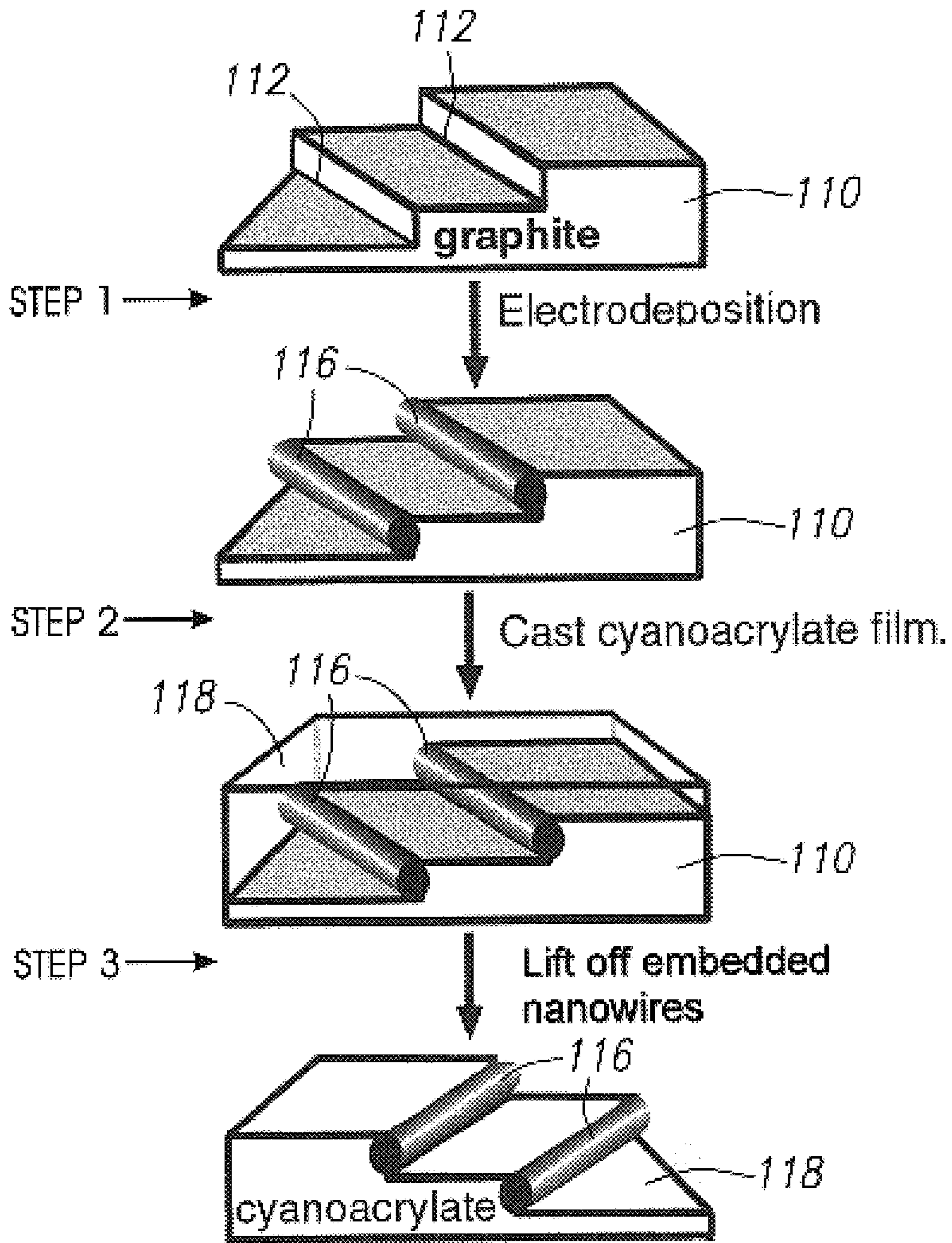


FIG. 6

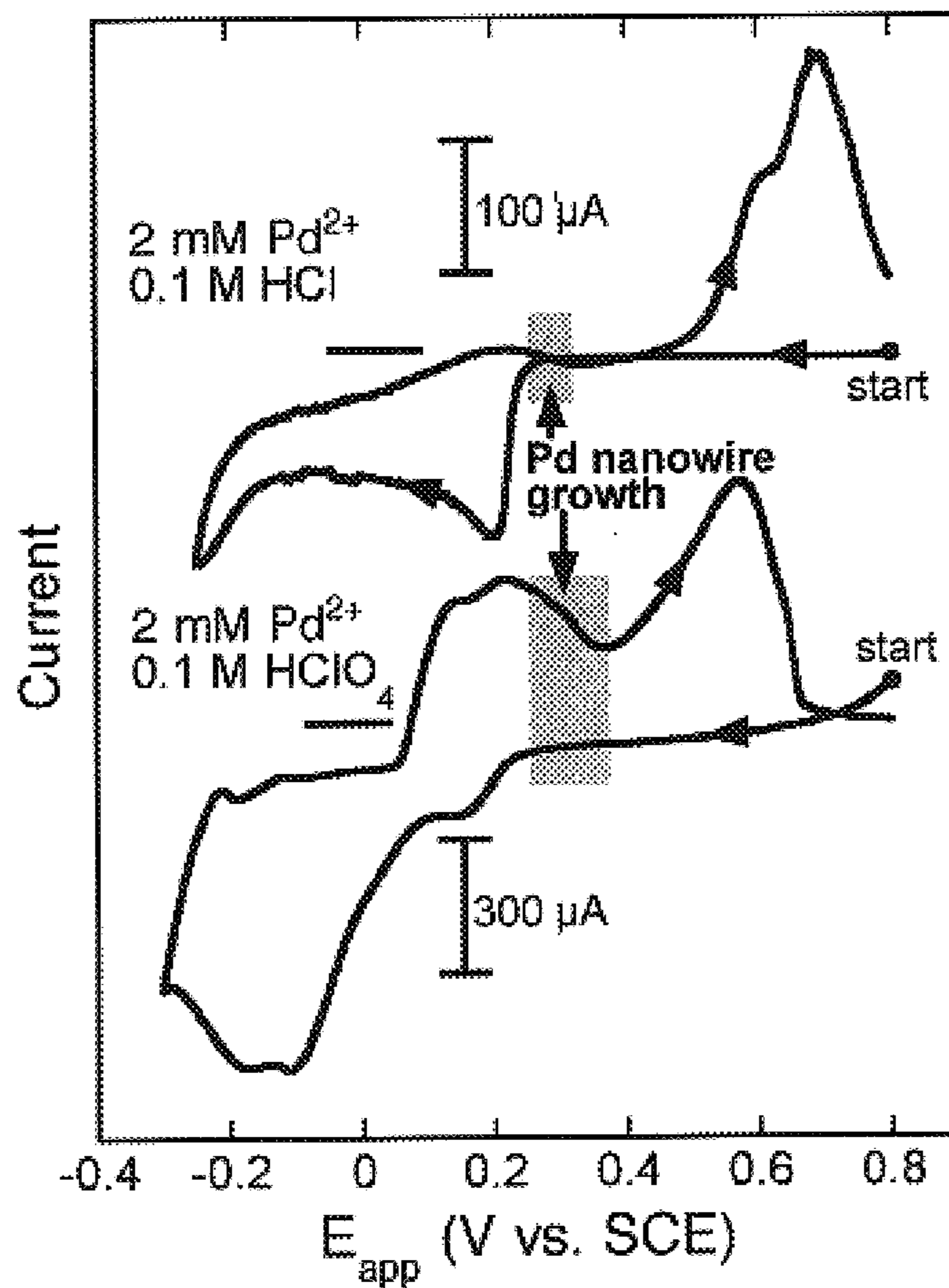


FIG. 7

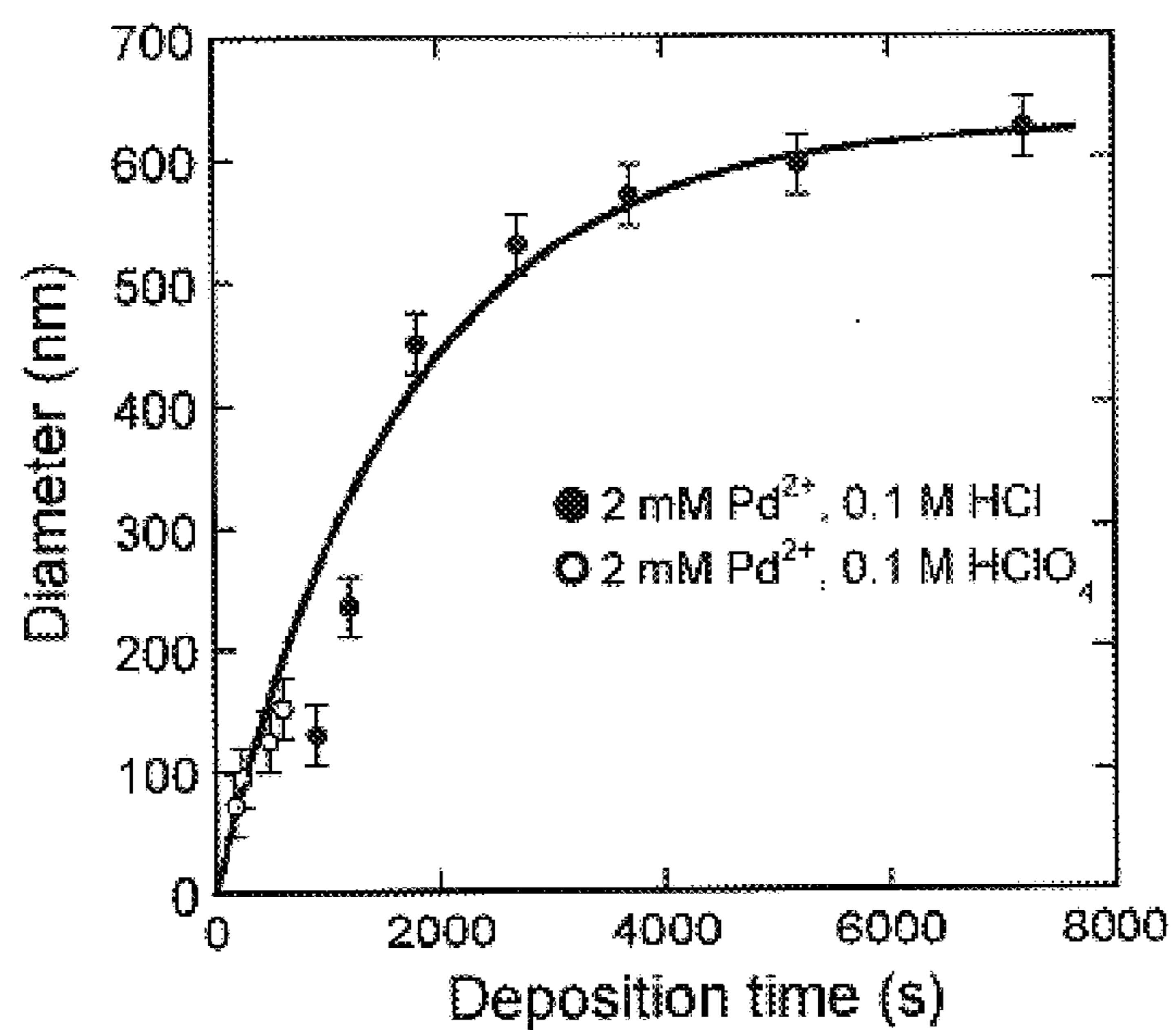


FIG. 8

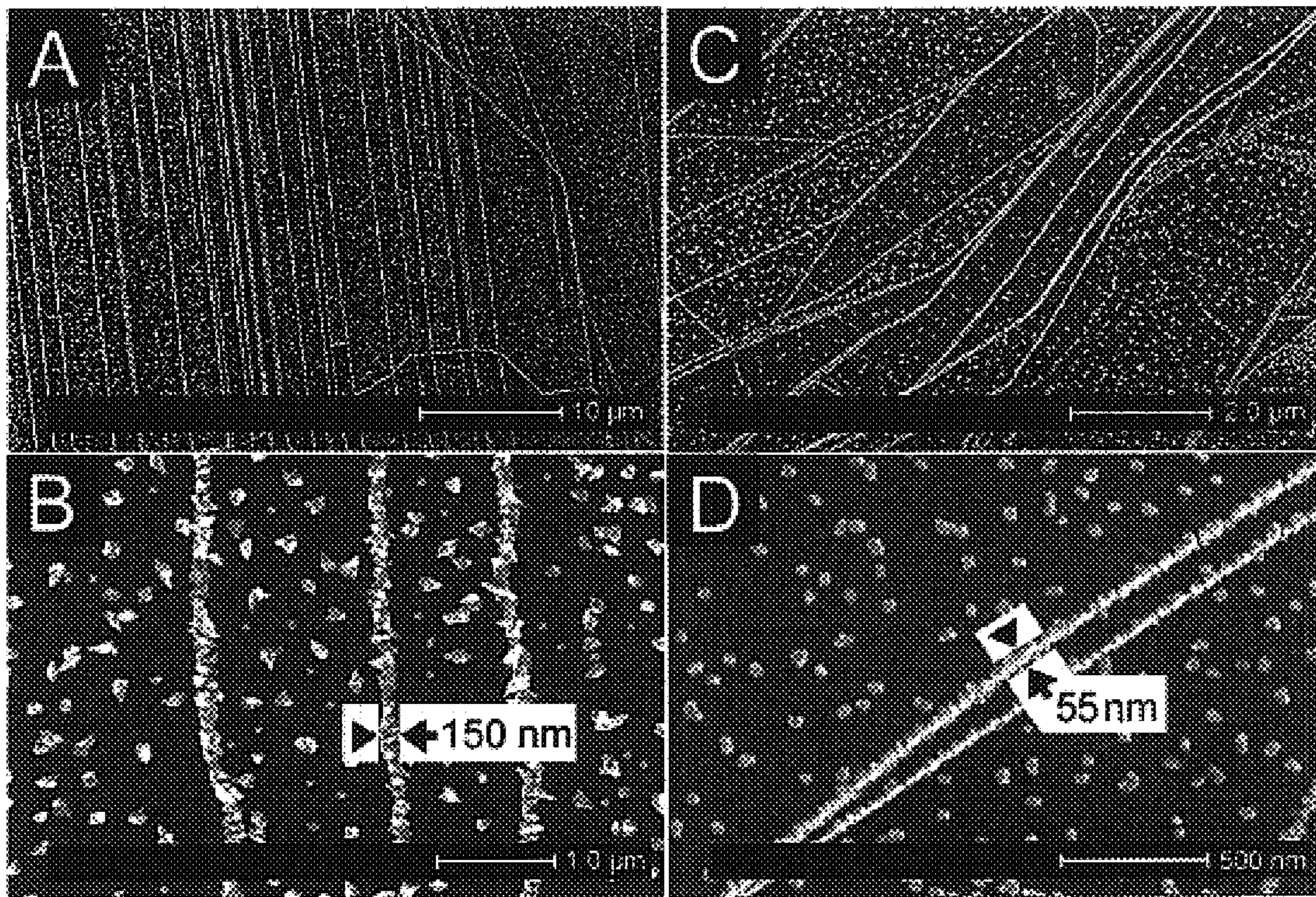


FIG. 9

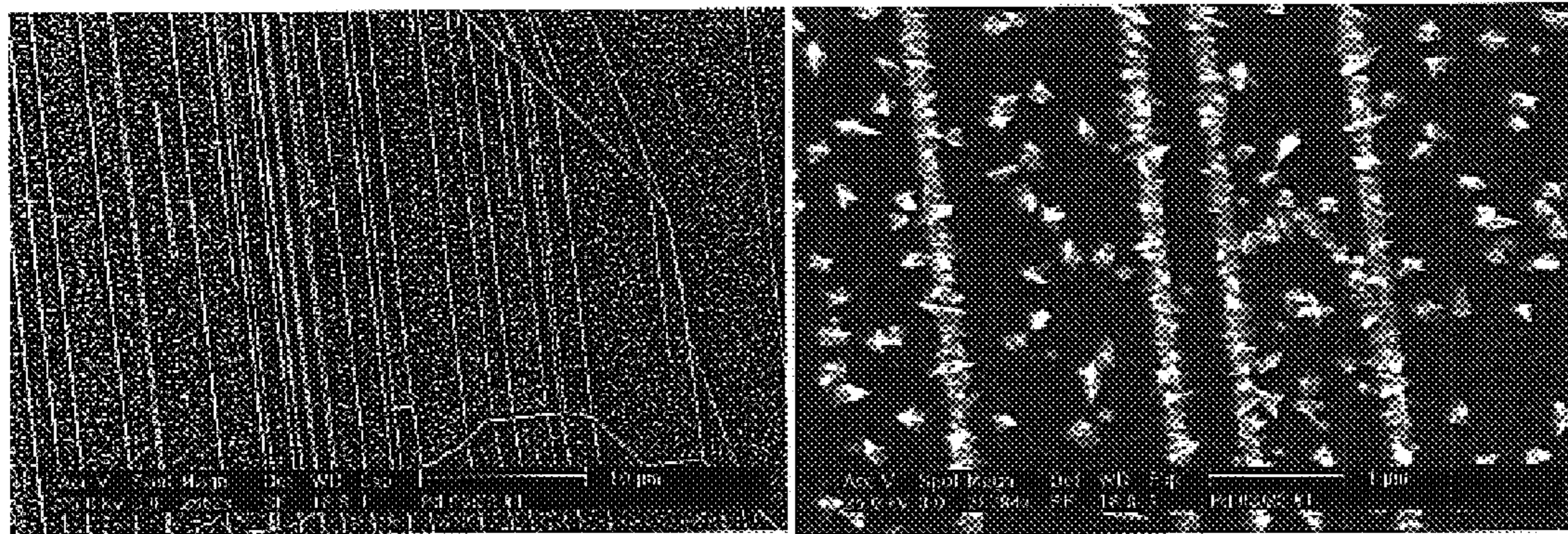


FIG. 10

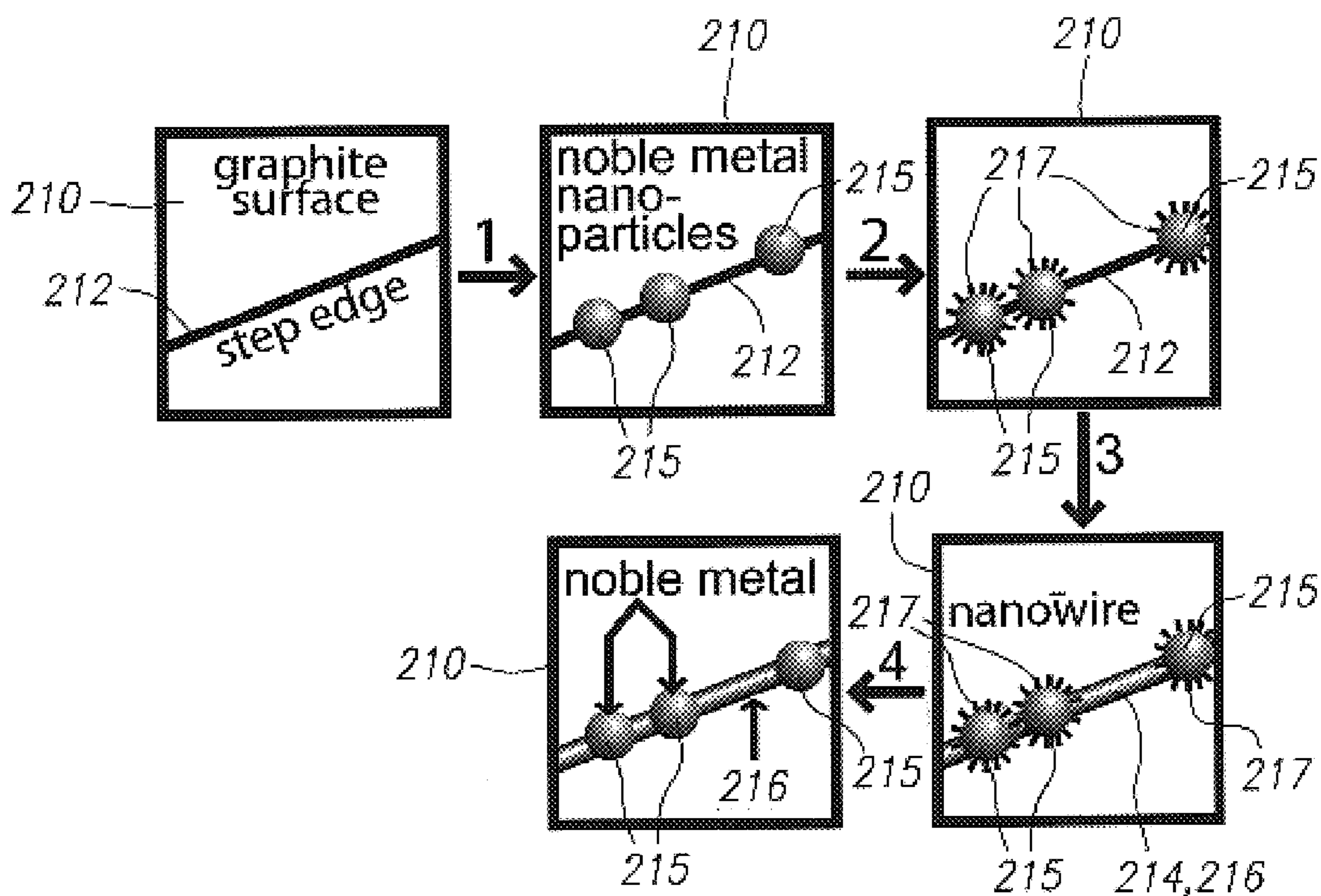


FIG. 11

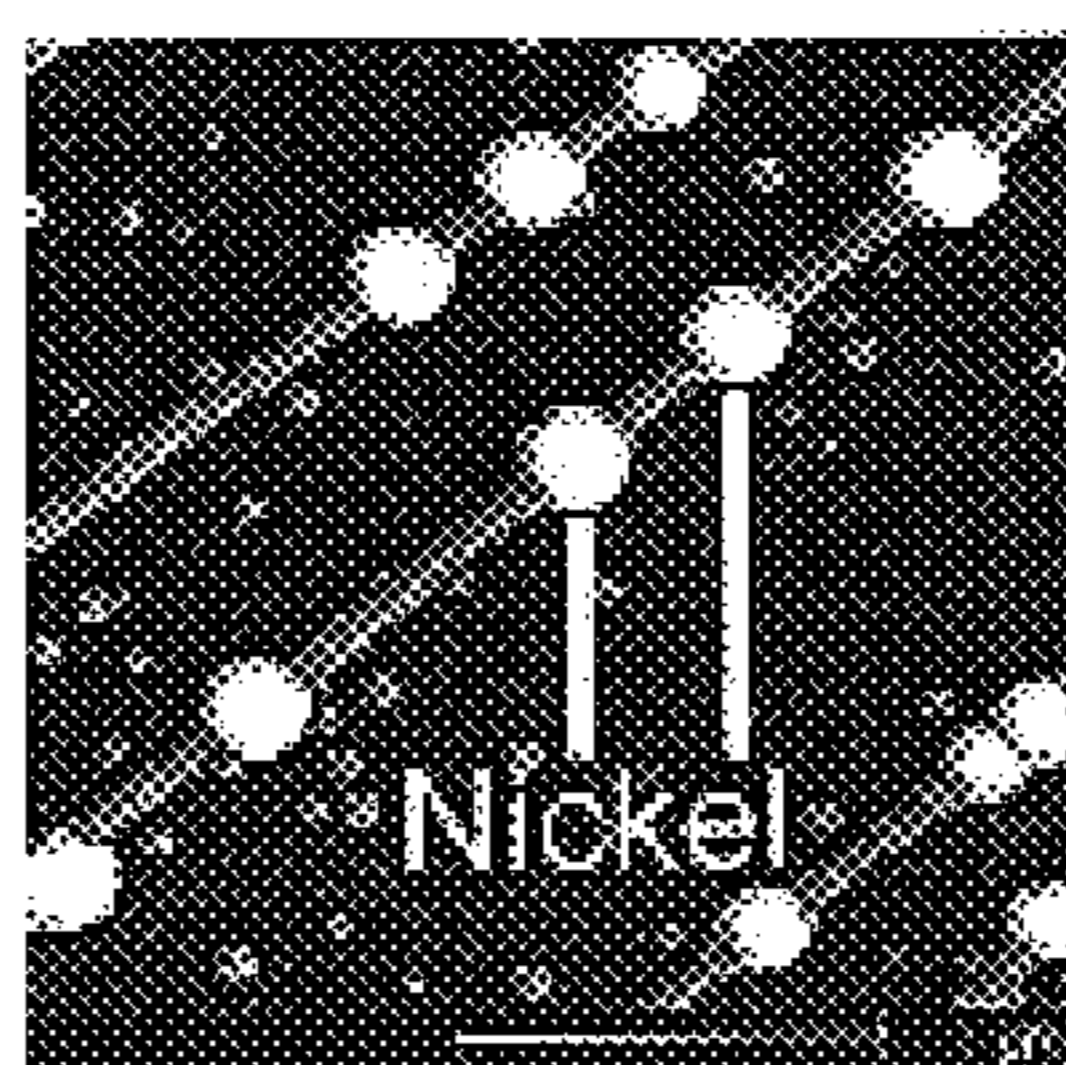


FIG. 12

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METHODS FOR FABRICATING METAL
NANOWIRESCROSS-REFERENCE TO RELATED
APPLICATION

This application is related to provisional U.S. patent application Ser. No. 60/306,715 filed Jul. 20, 2001 and Provisional U.S. patent application Ser. No. 60/317,862, filed Sep. 5, 2001 which applications are fully incorporated herein by reference.

This invention was made with Government support under contract no. DMR-9876479. The government has certain rights in this invention.

FIELD OF THE INVENTION

The invention relates to metal nanowires and, more particularly, to methods which facilitate the fabrication of long, free standing metal nanowires.

BACKGROUND

Metal nanowires have great potential for immediate use in small electronic circuits, sensitive chemical sensors or any application requiring metal filaments, and will likely be required as interconnects in the nanometer-scale electronics of the future, especially those future electronics which are not based on existing silicon technology. However, there are few methods for preparing nanowires that have such technological utility. More particularly, few methods are capable of producing nanowires that are long (i.e., greater than ten microns in length), uniform in diameter, free standing, and metallic. Two of the most successful approaches have been template synthesis and step-edge decoration.

The template synthesis method, which is described in publications by the research groups of M. Moskovits¹⁶⁻¹⁸, C. R. Martin⁸⁻¹⁵, and P. C. Searson²¹⁻²⁷, appears to permit the growth of metal nanowires over a wide range of diameters (from nanometer to micron scale) and for a variety of different metals. Template synthesis involves the growth of carbon, metals, or polymers in the void volumes of a nonconductive porous host such as polycarbonate ultrafiltration membranes, porous Al₂O₃ films, and track-etched mica crystals all of which possess long (microns or longer), dimensionally uniform pores. In general, these pores are oriented perpendicular to the plane of the porous film or membrane. Nanowires are produced by filling these pores with a conductive material. Template synthesis, however, is limited by its reliance on a template. Because all of the templates listed above possess linear, cylindrical (or prismatic) pores, only linear nanowires can be produced. Moreover, nanowires produced by template synthesis are limited to a maximum length that is equal to the thickness of the porous host membrane, which tends to range from 0.1 to 20 microns.

The step edge decoration method, which is described in publications by Himpfel³⁻⁴, Kern⁵⁻⁷, Behm² and others, involves the selective deposition of a metal or other material, such as CaF₂, at atomic step edges on a vicinal single crystal surface. Step edge decoration can be controlled to yield continuous "wires" of varied width and interwire spacing. Long nanowires that are many microns in length have been prepared. Because the dimension of the "wire" perpendicular to the vicinal surface has usually been limited to one or at most two atomic layers, it has not been possible to remove these ultra thin metallic ribbons from the surfaces on which they are synthesized. The technological utility of such nanowires is necessarily limited as a result.

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In view of the foregoing, it would be desirable to provide methods that facilitate the fabrication of nanowires that are metallic, long (i.e., greater than ten microns in length), uniform in diameter, and removable from the surface on which they are synthesized and, thus, free standing.

SUMMARY OF INVENTION

The present invention is directed to methods that facilitate the fabrication of nanowires that are metallic, long (i.e., greater than ten microns in length), uniform in diameter, and removable from the surface on which they are synthesized and, thus, free standing. The fabrication processes of the present invention provide an electrochemical route to dimensionally uniform and mechanically robust metal nanowires that range in diameter from approximately 10–15 nm to approximately 1.0 μ m, and are up to approximately 1.0 mm or more in length. The metal nanowires produced by the methods of the present invention advantageously exhibit wire diameter uniformity along the length of the wire as well as from wire-to-wire for thousands of nanowires. Preferably, the relative standard deviation from a mean diameter tends to be in a range of about 5 to 20%, and more preferably is no more than about 10%. In addition, the metal nanowires produced by the methods of the present invention tend to be electrically continuous along their entire length, i.e., typically less than about 5% of the wires produced by the methods of the present invention tend to show any visible breaks.

The present invention includes three interrelated step-decoration methods that are based on the selective electrodeposition of a metal or metal oxide from an aqueous solution at step edges present on a basal plane-oriented surface, such as graphite, that is exposed to the solution. In a first innovative aspect of the present invention (Method I), metal oxide from an aqueous solution is selectively electrodeposited along step edges present on the stepped surface to form precursor metal oxide wires. The metal oxide nucleates at a high linear density along the step edges forming beaded chains of metal oxide nuclei, which, with continued deposition, rapidly grow into a hemicylindrical nanowires. Wire growth involves low overpotential deposition at constant, or nearly constant, deposition current. Once formed, the precursor metal oxide nanowires are preferably reduced in hydrogen gas (H₂) at elevated temperatures to produce metal nanowires. Preferably this gas phase reduction occurs at about 500° C. for about an hour.

In a second innovative aspect of the present invention (Method II), metal nanowires are prepared by direct electrodeposition of metal from an aqueous solution along step edges present on a stepped surface exposed to the solution. Following a nucleation pulse, the metal nucleates at a high linear density along the step edges forming beaded chains of metal nuclei, which, with continued deposition, grow into hemicylindrical nanowires. Wire growth involves low overpotential deposition at constant, or nearly constant, low deposition current. The deposition rates according to this method are preferably extremely low, e.g., the deposition rate to prepare a palladium nanowire via direct electrodeposition having a 200 nm diameter was about 10 minutes and a 300 nm diameter was about 20 minutes.

In a third innovative aspect of the present invention (Method III), beaded or hybrid metal nanowires comprising a first metal (metal A) into which nanoparticles of a second metal (metal B) have been inserted are prepared by first electrodepositing nanoparticles of metal B selectively along step edges of a step surface. The metal B nanoparticles are

then capped with a molecular layer of an organic ligand having a strong affinity for the surface of the metal B nanoparticles. Metal A is then selectively electrodeposited along the step edges separating each metal B nanoparticle according to Method I or II. The ligand layer is preferably removed by heating the surface under reducing conditions in order to retain the metallic composition of the particles and connecting nanowire segments. The nanoparticles incorporated into the nanowires may range in diameter from the diameter of the nanowire itself, e.g., as small as about 10 nm, to about 1.0 μm or more.

In all three methods, the nanowires may be removed from the graphite surface by embedding the wires in a polymer film, and then peeling this film containing the embedded nanowires off of the graphite surface. This removal step makes the nanowires available for electrical characterization, for use as interconnects for connecting two nanometer-scale elements of a circuit, for the implementation of a variety of nanowire-based devices including sensors and biosensors, and for wiring of semiconductor quantum dots²⁰ to form a circuit. When used in sensors, the binding of an analyte molecule to the surface of the nanowire induces a measurable change in the nanowire conductivity.

Other objects and features of the present invention will become apparent from consideration of the following description taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic diagram of Method I of the present invention for preparing metallic nanowires.

FIG. 2 is a schematic diagram of a nanometer scale electric circuit incorporating an ensemble of metallic nanowires prepared in accordance with the methods of the present invention.

FIG. 3 is a series of scanning electron microscope images of molybdenum nanowires prepared in accordance with Method I of the present invention.

FIG. 4 is a typical cyclic voltammogram for MoO_4^{2-} at a highly oriented pyrolytic graphite electrode and scanning electron microscope images (above the cyclic voltammogram) of graphite surfaces obtained following the deposition of molybdenum dioxide (MoO_2).

FIG. 5 includes scanning electron microscope images of molybdenum nanowires embedded in a polystyrene film after removal from a graphite surface.

FIG. 6 is a schematic diagram of Method II of the present invention for preparing metallic nanowires by direct electrodeposition of a metal.

FIG. 7 includes cyclic voltammograms for a graphite electrode in two aqueous palladium plating solutions.

FIG. 8 is a graph showing the diameters of palladium nanowires as a function of the deposition time for nanowires deposited using the plating solutions indicated in FIG. 7.

FIG. 9 includes scanning electron micrographs of palladium nanowires prepared by electrodeposition from aqueous solutions indicated in FIG. 7.

FIG. 10 includes scanning electron micrographs of 300 nanometer diameter palladium nanowires prepared in accordance with Method II of the present invention.

FIG. 11 is a schematic diagram of Method III of the present invention for preparing hybrid or beaded metal nanowires.

FIG. 12 is a scanning electron micrograph image of a graphite surface following the implementation of the first three steps of Method III of the present invention.

DESCRIPTION

Referring in detail to the figures; methods that facilitate the fabrication of metallic nanowires and metallic nanowires prepared in accordance with the methods the present invention are shown. The methods of the present invention involve fabrication processes that provide an electrochemical route to dimensionally uniform, mechanically robust, long metal nanowires that are removable from the surface on which they are synthesized and, thus, free standing. The metal nanowires produced by the methods of the present invention tend to range in diameter from approximately 10–15 nm to approximately 1.0 μm and tend to be greater than 10–20 μm in length and preferably hundreds of microns in length on up to approximately 1.0 mm or more in length. The metal nanowires also advantageously exhibit high wire diameter uniformity along the length of the wire as well as from wire-to-wire for thousands of wires with a standard relative deviation from a mean diameter preferably in a range of about 5 to 20% and more preferably no more than about 10%. In addition, the metal nanowires produced by the methods of the present invention tend to be electrically continuous along their entire length, i.e., typically less than about 5% of the wires produced by the methods of the present invention tend to show any visible breaks.

The methods of the present invention include three inter-related step-decoration fabrication processes that are based on the electrodeposition of a metal or metal oxide from an aqueous solution on a basal plane-oriented surface, such as graphite, that is exposed to the solution. When suitable electric overpotentials are applied to the aqueous solution, the metal or metal oxide contained therein selectively deposits along the step edges present on the stepped surface forming “beaded-chains” of nuclei. With continued deposition, the beaded chains form three-dimensional nanowires with diameters in a range of about 10–15 nm to 1.0 μm for metal and in a range of about 20 nm to 1.3 μm for a metal oxide. The length of the nanowires tend to equal the length of the step edges on the stepped surface, which, with graphite in particular, tend to be equal to the grain diameter.

A first embodiment of the present invention, i.e., Method I, shown schematically in FIG. 1, includes a first step (Step 1) wherein precursor nanowires **14** are selectively electrodeposited along the step edges **12** present on a stepped surface **10** from a dilute, preferably alkaline (pH of approximately 8.5), aqueous plating solution. The plating solution preferably includes an electrodepositable metal oxide at concentrations between about $1 \times 10^{-3}\text{M}$ and about $10 \times 10^{-3}\text{M}$ of the metal ion of interest. The metal oxide in the plating solution tends to nucleate at an extremely high linear density, i.e., greater than approximately 20 nuclei/micron, along the step edges **12** forming “beaded chains” of metal oxide nuclei. With continued deposition, these beaded chains rapidly become smooth, hemicylindrical precursor nanowires **14**. As deposited, the precursor nanowires **14** tend to be brittle and nonconductive, but are highly uniform in diameter, with diameters in the range of about 20 nm to 1.3 μm , and tend to be hundreds of microns to about 1.0 mm or more in length.

Method I of the present invention includes a second step (Step 2) which involves a gas phase reduction of the precursor metal oxide nanowires **14** at elevated temperatures. Preferably, the metal oxide nanowires **14** are reduced in hydrogen gas (H_2) at about 500° C. for about one hour to produce metallic nanowires **16** that retain the dimensional uniformity and hemicylindrical shape of the precursor, or

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“parent”, metal oxide composite nanowires **14**. The metallic nanowires **16** tend to be smaller in diameter (about 10–15 nm to 1 μm) than the parent nanowires **14** by about 30 to 35%, and tend to be mechanically resilient and electronically conductive.

In a third step (Step **3**) of Method I, the gas phase reduced metal nanowires **16**, which tend to be only weakly associated with the stepped surface **10**, are embedded in a thin polystyrene film **18** that is cast onto the nanowires **16** and the graphite surface **10**. In a fourth step (Step **4**) of Method I, the film **18**, after it is allowed to air dry, is peeled off of the graphite surface **10** with the metal nanowires **16** embedded therein. The embedded nanowires **16** may comprise an ensemble of tens to hundreds of nanowires or more. The ensemble of nanowires **20**, which have been removed from the graphite surface **10** and, thus, are free standing, may advantageously be incorporated into an electronic circuit or sensor **22** as shown in FIG. **2**. Low impedance electrical contacts **24** of silver, evaporated gold film and the like, may be connected to the ends of the nanowires **20**.

Referring back to FIG. **1**, the system used for electrodeposition, i.e. Step **1**, preferably includes a glass electrochemical cell having a volume of approximately 50 mL. The plating solution noted above is introduced into the cell along with three electrodes: A platinum “counter” electrode, a reference electrode (e.g., saturated calomel electrode), and a “working” electrode, which is the surface, such as graphite, on which the nanowires are to be grown. The two additional electrodes—i.e., the counter and reference electrodes—enable high precision control of the potential of the working electrode. All three electrodes are preferably connected to a three-electrode potentiostat (e.g., EG&G Model 273A) which may be programmed to apply the required potential to the working electrode.

The selective decoration of the step edges **12** and, thus, wire growth, in Step **1** occurs when the deposition is carried out at suitable overpotentials, η_{dep} (where $\eta_{dep} = E_{dep} - E_{eq}$). Suitable overpotentials, η_{dep} , used in Step **1** for wire growth may range up to about (–)900 mV versus the reversible potential¹, E_{eq} , of the specific material involved. If the deposition is carried out using larger overpotentials, nucleation tends to be spatially indiscriminant and metal oxide particles tend to be deposited everywhere on the surface of the step terrace **13**. Moreover, if the overpotentials are too large, nucleation tends to occur on the surface of the step terrace **13** to the exclusion of the step edges **12**.

The deposition process of Step **1** is preferably further characterized by the application of a constant, or nearly constant, deposition current over the deposition period, which is typically greater than 20 seconds to grow nanowires of a desired size. Preferably, the constant deposition current is in a range of about 10 to 200 microamps/cm² of electrode area. This rate invariance is consistent with a convection limited growth process where natural convective mixing of the electrolyte near an electrode surface occurs. Under these conditions the rate law for growth of a hemicylindrical solid becomes

$$r(t) = (2i_{dep}t_{dep}M/\pi nF\rho L)^{1/2} \quad (1)$$

where $r(t)$ is the radius of the hemicylindrical nanowire, i_{dp} is the deposition current, t_{dep} is the deposition time, M is the atomic weight of the deposited metal, n is the number of electrons transferred per metal atom, F is the Faraday constant, i.e., 96,485 C eq⁻¹, ρ is its density, and L is the total length of the nanowire(s) on the electrode surface. As indicated by Equation 1, the nanowire diameter is directly

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proportional to the square root of the deposition time. As a result, nanowires of a particular diameter can be selectively produced by the methods of the present invention. Further, because dr/dt is proportional to $t^{-1/2}$, the growth of highly dimensional uniform structures, i.e., populations of nanowires that are narrowly dispersed with respect to wire diameter, is possible.

As indicated above, the diameter of the precursor nanowires **14** range from about 20 nm to 1.3 μm , which is typically many times the height of the step edge **12** responsible for nucleating the growth of the wire **14**. The height of the step edge **12** is typically about 0.3 to 2.0 nm. Two factors tend to contribute to this “amplification” of the step edge **12**. First, at the low deposition potentials used in the methods of the present invention, the incipient nucleation sites tend to be confined to the step edges **12** on the graphite surface **10**, which helps prevent the “spread” of the nanowire **14** onto terraces **13** during growth. The second factor is the inherent hemicylindrical symmetry of diffusional transport to metal nuclei arrayed along a linear step. The nanowire **14** ends up with a hemicylindrical cross-section because the ionic transport to the surface of the growing wire has this symmetry. These two factors operate in concert and permit the growth of hemicylindrical wires with virtually any diameter from step edges having molecular dimensions.

It should be understood that Method I may be used to produce metal nanowires from any conductive metal oxide that is electrodeposable, including MoO_2 , Cu_2O , Fe_2O_3 , and the like. The fabrication of molybdenum nanowires is described below with regard to FIGS. **3–5** for exemplary purposes only. See also Zach et al., *Science* 290 (2000) 2120²⁸, which is incorporated by reference as if set forth in full.

To prepare molybdenum nanowires in accordance with Method **1** shown in FIG. **1**, molybdenum dioxide (MoO_2) is first electrodeposited (Step **1**) according to the reaction:



Under the conditions employed in Step **1**, i.e., low overpotentials in a range of about –600 mV to –800 mV and constant, or nearly constant, deposition current in a range of about 10 to 200 microamps/cm², MoO_2 nucleates at an extremely high linear density (greater than about 20 nuclei/ μm) along the step edges **12**. The deposited MoO_2 forms “beaded chains” of 5–8 nm diameter MoO_2 nuclei which, with continued deposition, rapidly become smooth, hemicylindrical nanowires. FIG. **3** shows a series of MoO_2 nanowires electrodeposited according to Step I of Method **1** along step edges of a stepped graphite surface. As shown in FIG. **3**, the MoO_2 nanowires include nanowires with diameters of 13 nm, 62 nm, 130 nm and 210 nm. The numbers at the upper left indicate the deposition time, in seconds, i.e., 1s, 4s, 16s, and 256s, for preparing these MoO_2 nanowires from an aqueous solution containing 1.0 mM MoO_4^{2-} by applying a deposition potential of about –0.75 V vs. SCE.

A typical cyclic voltammogram for MoO_4^{2-} at a highly oriented pyrolytic graphite electrode is shown in FIG. **4**. As FIG. **4** indicates, the selectivity of MoO_2 nucleation is controlled by the deposition potential. The scanning electron microscopy (SEM) images (above the cyclic voltammogram) of the graphite surfaces were obtained following deposition at potentials in a range of about (–)0.7 to (–)0.9 V versus a saturated calomel electrode (SCE) (right) and in a range of about (–)1.25 to (–)1.4 V versus SCE (left). As shown, electrodeposition of MoO_x , which has a reversible potential of about 0.1V, occurred with a high degree of selectivity at step edges at deposition overpoten-

tials in the range of (-)0.6 to (-)0.8 V versus SCE (right). The application of a deposition potential more negative than (-)1.0 V (left) caused particle growth at surface terraces.

Once formed, MoO_x nanowires may be reduced in H_2 at 500°C . to produce metallic molybdenum (Mo^0) nanowires (Step 2). These metal nanowires are smaller in diameter by about 30% to 35% as compared with the parent MoO_x wires, and are only weakly associated with the graphite surface 10. Removal of these reduced wires from the graphite surface is accomplished by embedding the nanowires in a polystyrene film (Step 3), and lifting this film together with the embedded nanowires off the graphite surface (Step 4). FIG. 5 provides SEM images of molybdenum nanowires embedded in a polystyrene film after removal from a graphite surface. The ability to remove molybdenum nanowires from the graphite surfaces on which they are synthesized facilitates the technological utility of these nanostructures both in electronic devices, as interconnects, and in sensors.

Turning to FIG. 6, a second embodiment of the present invention, Method II, is shown schematically to involve the preparation of metal nanowires by "direct" electrodeposition of a metal on a stepped surface 110, such as graphite, that is exposed to an aqueous solution containing the metal. In a first step (Step 1), nanowires 116 are selectively electrodeposited along the step edges 112 present on a stepped surface 110 from an aqueous plating solution comprising an electrodepositable metal. The solution preferably includes metals such as palladium, gold and the like, at concentrations between about 1×10^{-3} and 10×10^{-3} M of the metal ion of interest. Electrodeposition of gold, however, is preferable performed in an electrochemical cell that is pressurized to about 40 atm. Following a nucleation pulse, the metal in the plating solution nucleates at an extremely high linear density (i.e., greater than about $20/\mu\text{m}$) along the step edges 112 forming "beaded chains" of metal nuclei, which, with continued deposition, become smooth, hemicylindrical nanowires 116.

Preferably, the electrodeposition is carried out at very low deposition overpotentials of up to about (-)400 mV and preferably in a range of about (-)10 to (-)200 mV. To increase nucleation density and, thus, ensure that the nanowires are continuous, a nucleation pulse, well negative of the reversible potential, may be applied for about five milliseconds prior to electrodeposition at the desired overpotential. The deposition is preferably carried out at low constant, or nearly constant, deposition current, e.g., preferably less than 50 mA/cm^2 . Depending on the metal being deposited and the applied current density, which is preferably in a range of about $5\ \mu\text{Acm}^{-2}$ to $50\ \mu\text{Acm}^{-2}$, the deposition rates in Method II are preferably extremely low. For example, as shown in FIG. 8 and discussed below, the deposition time to prepare a palladium nanowire having a 200 nm diameter was about ten minutes. Deposition rates to prepare metal nanowires of a desired diameter may be determined according to Method II may be calculated using Equation (1).

In a second step (Step 2) of Method II, the metal nanowires 116 are embedded in a thin polystyrene film 118 that is cast onto the nanowires 116 and the graphite surface 110. In a third step (Step 3), the film 118, after it is allowed to air dry, is peeled off of the graphite surface 110 with the metal nanowires 116 embedded therein. The embedded nanowires 16 may comprise an ensemble of tens to hundreds of nanowires or more. The ensemble of nanowires, which have been removed from the graphite surface 110, may also advantageously be incorporated into an electronic circuit or sensor 22 as shown in FIG. 2.

Palladium nanowires prepared in accordance with Method II are described in regard to FIGS. 6-10 for exam-

plary purposes only. Palladium nanowires may be electrodeposited from aqueous solutions containing palladium. Examples of such solutions include 2.0 mM Pd^{2+} , 0.1 M HCl, water, and 2.0 mM Pd^{2+} , 0.1 M HClO_4 , and the like. Palladium nanowires prepared by the process of Method II are shown in FIGS. 9-10. Starting with a freshly cleaved graphite surface within a palladium plating solution, these nanowires were prepared by first applying a 5 ms nucleation pulse of -0.2 V (vs. saturated calomel electrode, SCE). As shown in FIG. 7, this potential is well negative of the reversible potential for palladium deposition in these solutions (+0.6 to +0.7 V vs. SCE). After this nucleation pulse, the growth of palladium nanowires was carried out using potentials in the ranges shown in gray in FIG. 7. These deposition potentials produce deposition current densities ranging from about $30\text{--}60\ \mu\text{A cm}^{-2}$ and deposition times for 200 nm diameter wires of about 10 minutes (see FIG. 8). The deposition times for palladium nanowires having 300 nm diameters, as shown in FIG. 10, were about 20 minutes.

The morphology of the palladium nanowires, as well as other metal nanowires, obtained by electrodeposition tends to be dependent on the identity of the electrolyte present in the plating solution. For example, palladium nanowires deposited from HCl solutions, as shown in FIG. 9 (left), tend to be rough and granular. The dimensions of the grains in these polycrystalline wires as estimated from SEM images ranged from about 50 to 300 nm. Continuous nanowires of 150 nm in diameter have been obtained from this solution. Deposition of palladium nanowires from HClO_4 solutions as shown in FIG. 9 (right), yield nanowires having a smoother morphology. The grains in these nanowires were 10-50 nm in diameter. A smoother morphology permits nanowires as narrow as 55 nm in diameter to be deposited. The rough and smooth nanowires prepared using these two plating solutions behave electrically identical to one another.

A third embodiment of the present invention, Method III, involves the preparation of beaded or hybrid metal nanowires comprising a first metal (metal A) into which nanoparticles of a second metal (metal B) have been inserted. These hybrid metal nanowires are prepared, as shown schematically in FIG. 11, by first (Step 1) electrodepositing nanoparticles 215 of metal B selectively along step edges 212 of a stepped surface 210 such as graphite. The metal B nanoparticles 215, which are preferably formed from a noble metal including nickel, palladium, platinum, gold, and the like, are electrodeposited, e.g., from an aqueous solution comprising 1.0×10^{-3} M to 10×10^{-3} M of the metal ion of interest using a suitable overpotential. Platinum nanoparticles, for example, are preferably deposited for 100 ms from a 1.0×10^{-3} M Pt^{2+} solution using an overpotential of -0.5V in order to obtain 10 nm diameter metal nanoparticles at a density of about 10^8 to $10^{10}\ \text{cm}^{-2}$. See, e.g., Zach et al., *Adv. Mat.*, 12 (2000) 878²⁹ and Zoval et al., *J. Phys. Chem. B*, 102 (1998) 1166³⁰, and others which are incorporated by reference as if set forth in full.

The deposited metal B nanoparticles 215 are then (Step 2) exposed to an ethanolic solution of an alkane thiol. As a result of the thiol exposure, each nanoparticle is "capped" by a self assembled molecular monolayer of an organic ligand 217 having a strong affinity for the surface of the metal B nanoparticles 215. Examples of such ligands include Thiols (chemical formula: R-SH where R is a hydrocarbon), which have an affinity for noble and coinage metals including Pt, Pd, Au, Ag, and Cu, and Nitriles (chemical formula: R-CN where R is a hydrocarbon), which have an affinity for Pt, Pd and Ag.

In a next step (Step 3), a metal A or a metal A oxide is selectively electrodeposited along the step edges 212 sepa-

rating each metal B nanoparticle **215** according to Method I or II discussed above to form a metal A or metal A oxide nanowire **214**, **216** between the metal B nanoparticles **215**. Because the ligand **217** forms an electrically insulating layer atop of the metal nanoparticles **215**, the deposition of the wire material does not occur on top of the nanoparticles **215**, just between the nanoparticles **215**.

In a final step (Step **4**), the ligand layer **227** is preferably removed by heating the surface under reducing conditions in order to retain the metallic composition of the particles **215** and connecting nanowire segments **216**. Preferably, the reduction of the surface occurs in H₂ at 500° C., which results in the alkane thiol being pyrolysed. The nanoparticles incorporated into the nanowires may range in diameter from the diameter of the nanowire itself, e.g., as small as about 10 nm, to about 1.0 μm or more. FIG. **12**, which is a SEM image of a graphite surface following Step **3** of Method III, shows hybrid nanowires comprising nickel nanoparticles and molybdenum dioxide nanowire segments prepared according to Method III.

Like the metal nanowires prepared according to Methods I and II (see FIGS. **1** and **6**), the hybrid nanowires prepared according to Method III may be removed from the graphite surface by embedding the wires in a polymer film, and then peeling this film containing the embedded nanowires off of the graphite surface. Because the hybrid nanowires are removable they may be utilized as elements of nanometer-scale circuits, sensors, biosensors, and the like. When used in sensors, the nanowire segments are employed to “read-out” any measurable change in the nanoparticle conductivity induced by the binding of an analyte molecule to the surface of the nanoparticle.

While the invention is susceptible to various modifications and alternative forms, specific examples thereof have been shown in the drawings and are herein described in detail. Many alterations and modifications can be made by those having ordinary skill in the art without departing from the inventive concepts contained herein. It should be understood, therefore, that the illustrated embodiments have been set forth only for the purposes of example and that they should not be taken as limiting the invention.

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What is claimed is:

1. A method for preparing metallic nanometer scale wires comprising the steps of
 - electrodepositing a plurality of wires from an aqueous solution including a metal at step edges present on a stepped surface,
 - embedding the plurality of wires in a polymer film, and
 - lifting the plurality of wires off of the stepped surface.
2. The method of claim 1 wherein the electrodepositing step includes applying a nucleation pulse to the aqueous solution.
3. The method of claim 2 wherein the electrodepositing step further includes applying a deposition potential to the aqueous solution.
4. The method of claim 3 wherein the over potential corresponding to the deposition potential is less than about –400 millivolts.
5. A method for preparing metallic nanowires comprising the steps of
 - electrodepositing metal oxide particles at step edges present on a stepped surface from an aqueous solution including a metal oxide forming a plurality of metal oxide wires,
 - reducing the plurality of metal oxide wires via gas phase reduction to a plurality of metal wires,
 - embedding the plurality of metal wires in a polymer film, and
 - lifting the plurality of metal wires from the stepped surface.
6. The method of claim 5 wherein the electrodepositing step includes applying a deposition potential to the solution.
7. The method of claim 6 wherein the over potential corresponding to the deposition potential is less than –900 millivolts.
8. The method of claim 5 wherein the reducing step includes reducing the plurality of metal oxide wires in hydrogen gas.
9. The method of claim 8 wherein the reducing step further includes reducing the plurality of metal oxide wires at about 500° C.
10. A method for preparing beaded nanowires comprising the steps of
 - electrodepositing nanoparticles of a first metal from a first aqueous solution at step edges present on a stepped surface, and
 - electrodepositing wire segments of a second metal from a second aqueous solution at the stepped edges between the nanoparticles forming a plurality of beaded nanowires.

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11. The method of claim **10** wherein the first metal is a noble metal.

12. The method of claim **10** further comprising the step of capping the nanoparticles with a ligand.

13. The method of claim **12** further comprising the step of heating the nanoparticles and wire segments of the plurality of beaded nanowires at reduction conditions.

14. The method of claim **13** further comprising the step of embedding the plurality of beaded nanowires in a polymer film.

15. The method of claim **13** further comprising the step of removing the plurality of beaded nanowires from the stepped surface.

16. A method for preparing nanometer scale metallic wires comprising the steps of

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applying a deposition potential to an aqueous solution comprising a metal or metal oxide wherein the deposition potential corresponds to an over potential of less than -900 millivolts, and

selectively depositing metal or metal oxide nanowires at step edges present on a stepped surface.

17. The method of claim **16** further comprising the step of reducing the metal oxide nanowires in hydrogen gas.

18. The method of claim **17** wherein the reducing step includes reducing the metal oxide nanowires in hydrogen gas at about 500° C.

19. The method of claim **16** further comprising the step of embedding the metal nanowires in a polymer film and removing the metal nanowires from the stepped surface.

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